Anna Kisko

MICROSTRUCTURE AND PROPERTIES OF REVERSION TREATED LOW-Ni HIGH-Mn AUSTENITIC STAINLESS STEELS
ANNA KIKKO

MICROSTRUCTURE AND PROPERTIES OF REVERSION TREATED LOW-Ni HIGH-Mn AUSTENITIC STAINLESS STEELS

Academic dissertation to be presented, with the assent of the Doctoral Training Committee of Technology and Natural Sciences of the University of Oulu, for public defence in the Wetteri auditorium (IT115), Linnanmaa, on 10 June 2016, at 12 noon

UNIVERSITY OF OULU, OULU 2016
Abstract

In this thesis, the influence of reversion and recrystallization annealing on microstructure and mechanical properties was studied in metastable austenitic low-Ni high-Mn stainless steels, some alloyed with up to 0.45 wt.% Nb. Further, the effect of the various microstructures created by reversion and recrystallization on strain-induced martensite transformation in tensile testing was investigated. The aim was to achieve excellent combinations of strength and ductility in the steels and to improve understanding of the behaviour of ultrafine-grained austenitic stainless steels during deformation. All the steels were cold-rolled up to 60% thickness reduction producing up to 60% strain-induced α'-martensite in the austenitic structure. Annealing was carried out using a Gleeble thermomechanical simulator between 450–1100 °C for durations of 0.1–1000 s. The resultant microstructures were examined using different research equipment and methods.

Regardless of the amount of Nb alloying, shear- and diffusion-controlled reversion could be completed by annealing at 700 °C, although at this temperature no recrystallization of the untransformed cold-rolled austenite occurred. At 800 °C, however, the cold-rolled austenite recrystallized, producing a non-uniform grain structure comprising ultrafine-grained areas formed via reversion and coarser ones formed by recrystallization of the retained austenite. At 900 °C, a uniform fine austenite grain size of about 2 μm was obtained. At higher annealing temperatures of 1000–1100 °C, normal grain growth of fine grains took place during prolonged annealing in steel with no Nb. However, grain growth was effectively retarded by alloying with 0.28 wt.% Nb.

The non-uniform structures consisting of reverted and retained austenite exhibited excellent combinations of yield strength and uniform elongation. The results also showed that tensile strain-induced martensite nucleation sites and α'-martensite formation vary in a complex way depending on grain size.

Keywords: austenitic stainless steel, grain size refinement, niobium alloying, reversion and recrystallization annealing, strength
Kisko, Anna, Reversiokäsitteltyjen matalanikkelen, korkeamangaanisten austeniittisten ruostumattomien terästen mikrorakenteen ja ominaisuuksien \textit{Tiivistelmä}

Väitöstyössä tutkittiin reversiohehkutuksen vaikutusta metastabiilin 1\% nikkeliä ja 9\% mangaanisia sisältävien austeniittisten ruostumattomien terästen mikrorakenteeseen ja mekaanisiin ominaisuuksiin sekä austeniitin raekoon ja mikrorakenteen vaikutusta muokkasmartensiitiin syntyyn vetokokeessa. Koeteräksistä osa oli lisäksi niobiseostettuja. Tavoitteena oli nostaa terästen lujuutta ja ymmärtää ultrahienorakeisen austeniittisen ruostumattomien terästen käyttäytymistä muokkauksessa. Teräkset kylmänkuukattiin 60\% valssausreduktiolla, jolloin austeniitin rakenteeseen muodostui muokkasmartensiitit enimmillään 60\%. Reversiohehkutukset tehtiin Gleeble termomekaanisella simulaaattorilla lämpötiloisissa 450–1100 °C j ja 0.1–1000 s pitäjöillä. Saatuja mikrorakenteita tutkittiin eri tutkimuslaitteistoilla ja -menetelmissä.

700 °C hehkutuksessa leikkautumala ja diffuusion väilityksellä tapahtuva reversio oli nopea myös niobi-seostetuilla teräksillä, mutta rekristallisaatiodessa ei tapahtunut. 800 °C hehkutuksessa muokkauksessa teräksillä jäänyt austeniiti rekristallisoi, mutta raerakenteen muodostus epätasaisesti koostuen reversiopidemmasta ultrahienorakeista ja jäännösausten tilin rekristallisointi tapahtuu karkeampiin raseihin. Sitä vastoin hehkutus 900 °C:ssa tapahtui tasainen 2 μm rasteraan raekoon. Pitkissä hehkutuksissa korkeammissa lämpötiloisissa 1000–1100 °C niobi-seostumattomissa teräksillä tapahtui hienojen raseiden normaalioikeen kasvua. Kuitenkin 0.28p-% niobi-seostukseen havaittiin oleva riittävä estäminen raseen kasvua.

Reversiopidemmat ja osittaisen rekristallisointi tapahtuivat raerakenteilla saatiin erinomaiset myöät-lujuus-tasavennymäyhdistelmät. Vetokokeissa martensiitiin ydintymispaikat ja -nopeus vaihtelivat monimuutoksessa tavalla raekosta riippuen.

\textit{Asiasanat:} austeniitinen ruostumaton teräs, lujuus, niobiseostus, raekoon hienonnan, reversiopidemmat ja rekristallisointihehkutus
Acknowledgements

This thesis comprises work carried out in 2010–2015 in the Materials Engineering and Production Technology research unit of the Centre for Advanced Steels Research (CASR) at the University of Oulu. The research was funded by the University of Oulu Graduate School on Advanced Materials Doctoral Programme (ADMA-DP) and the Finnish Funding Agency for Technology and Innovation (Tekes) as a part of the Light and Efficient Solutions program (LIGHT) of the Finnish Metals and Engineering Competence Cluster (FIMECC Ltd). The experimental materials were provided by Outokumpu Oyj. This thesis was also supported by scholarships awarded by the Jenny ja Antti Wihuri Foundation, the KAUTE foundation, Metallinjalostajien rahasto, Tauno Tönningin säätö, Tekniikan Edistämissäätiö (TES) and the Walter Ahlström Foundation.

During this project I have received guidance and support from several experts and other people whom I would like to acknowledge. I would like to thank my supervisor, Professor David Porter, for his guidance and support in my research. I would like to present my sincere gratitude and best thanks to Professor Emeritus Pentti Karjalainen for his scientific supervision, kindness and suggestions for improving the quality of my research and papers during this entire work.

I would like to express my gratitude to Dr. Juho Talonen of Outokumpu Oyj for his extremely valuable comments throughout the research project. I also wish to thank Professor Anthony DeArdo from the University of Pittsburgh, Professor Devesh Misra from the University of Louisiana at Lafayette, Assistant Professor Puspendu Sahu from Jadavpur University, Associate Professor Atef Hamada from Suez University and Dr. Ludovica Rovatti from Polytechnic University of Milan for their contributions to the published papers. I would also like to thank Professor Paulo Ferreira from the University of Texas at Austin and Professor Ahmad Kermanpur from Isfahan University of Technology for the pre-examination of this thesis and for the suggestions for improving the manuscript.

I express my thanks to my colleagues in the Materials Engineering Research Group. I especially thank Dr. Saara Mehtonen for her peer support.

Finally, I would like to thank my friends and family, especially my Mom, Dad and sister Kaisa, for their endless support. I thank my dearest Pasi and Pauli for encouragement in every precious moment during these years.

Oulu, April 2016

Anna Kisko
Symbols and abbreviations

Af  Austenite finish temperature [°C]
Ag  Uniform elongation [%]
As  Austenite start temperature [°C]
d  Average grain size [μm or nm]
D  Average radius of the grains [μm]
d0 Initial grain size [μm]
f  Volume fraction of particles
F_d Driving force for grain growth [MPa]
F_p Pinning force for grain growth [MPa]
\(\Delta G_{\text{activation}}\) Activation energy for grain growth [J/mol]
\(\Delta G_{MS}^{\gamma' - \gamma}\) Free energy difference between austenite and martensite [J/mol]
k  Constant (page 30)
k  Grain growth kinetic parameter (page 29)
k0 Material constant
Md Upper limit for strain-induced transformation
Ms Martensite start temperature
n  Grain growth exponent
N  Number of measured particles
r  Radius of the spherical particles [nm]
R  Gas constant [J/(K mol)]
Rp0.2 Yield strength [MPa]
Rm Tensile strength [MPa]
t  Annealing time [s]
T  Annealing temperature [K] (Equation 2)
T  Annealing temperature [°C] (except Equation 2)
T0 Temperature, where austenite and martensite are in thermodynamic equilibrium
W  Width [mm]
W0 Initial width [mm]
\(\alpha'\) Alpha prime (used to denote martensite as opposed to \(\alpha\) for ferrite)
\(\gamma\) Austenite
\(\gamma\) Grain boundary energy [J/m²] (page 29)
\(\varepsilon\) Epsilon-martensite
\(\sigma_y\) Yield strength [MPa]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_0$</td>
<td>Yield strength without grain boundaries [MPa]</td>
</tr>
<tr>
<td>CG</td>
<td>Coarse austenite grains (&gt; 18 $\mu$m)</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron backscatter diffraction</td>
</tr>
<tr>
<td>FBM</td>
<td>Flexible boundary model</td>
</tr>
<tr>
<td>FEG-SEM</td>
<td>Field emission gun scanning electron microscope</td>
</tr>
<tr>
<td>FETEM</td>
<td>Field emission transmission electron microscope</td>
</tr>
<tr>
<td>FG</td>
<td>Fine austenite grains (~4 $\mu$m)</td>
</tr>
<tr>
<td>MG</td>
<td>Micron-scale austenite grains (~1.5 $\mu$m)</td>
</tr>
<tr>
<td>LOM</td>
<td>Light optical microscope</td>
</tr>
<tr>
<td>RA</td>
<td>Retained austenite</td>
</tr>
<tr>
<td>SFE</td>
<td>Stacking fault energy</td>
</tr>
<tr>
<td>SHR</td>
<td>Strain hardening rate</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>UFG</td>
<td>Ultrafine austenite grains (~0.5 $\mu$m)</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
List of original publications

This thesis is based on the following publications, which are referred to throughout the text by their Roman numerals:


Anna Kisko has been the main and corresponding author of all the publications. She has planned the tests and performed all the experiments, except the Gleeble annealings for Papers I–VI, the tensile tests for Papers I and II, the TEM examinations for Papers II, III and VI, the XRD runs for Papers III and IV and the dislocation density analysis for Paper III. She has also done the data analysis. Juho Talonen and Pentti Karjalainen have commented on the contents of Papers I–VI and David Porter on Papers IV and V.

Paper I is an overall, comprehensive study of the microstructures and properties of reversion-treated 15Cr-9Mn-1Ni-2Cu (coded 0Nb) steel. It compares the enhanced mechanical properties with conventional values (reported in the materials standards) and other steels.

In Paper II, the microstructure and formed anisotropy of mechanical properties of the 0Nb steel in the temper-rolled stage and the annealed stage are discussed.
Paper III focuses on $\alpha'$-martensite transformation during reversion annealing of the 0Nb steel. The properties of $\alpha'$-martensite, formed during cold rolling or annealing, was studied.

In Paper IV, the reversion mechanisms, recrystallization of retained austenite and mechanical properties of the 0Nb and Nb-alloyed 0.28Nb and 0.45Nb steels are described in detail. Hall-Petch analysis was carried out and the strengthening mechanisms of the steels were discussed.

Paper V focuses on grain growth in the 0Nb, 0.05Nb, 0.11Nb, 0.28Nb and 0.45Nb steels during prolonged, high-temperature annealing. Driving and pinning forces for grain growth are calculated and the grain growth behaviour of the steels is explained.

Paper VI discusses $\epsilon$- and $\alpha'$-martensite nucleation sites and volume fraction of $\alpha'$-martensite at the beginning of tensile straining in the reversion-treated 0Nb steel with various grain structures, i.e., reverted grains and retained austenite, micron-sized grains and retained austenite, fine-grained austenite and coarse-grained austenite.
# Table of contents

**Abstract**  
**Tiivistelmä**  
**Acknowledgements**  
**Symbols and abbreviations**  
**List of original publications**  
**Table of contents**  

1 **Introduction**  
1.1 Preface ......................................................... 15  
1.2 Plastic deformation of metastable austenitic stainless steels .......... 16  
  1.2.1 Thermodynamics of strain-induced martensite transformation ......................................................... 16  
  1.2.2 Stacking faults, ε-martensite and deformation twinning .......... 18  
  1.2.3 α’-martensite .......................................................... 19  
1.3 Reversion, recrystallization and grain growth ......................... 20  
  1.3.1 Reversion mechanism ........................................... 20  
  1.3.2 Factors affecting reversion ....................................... 20  
  1.3.3 Recrystallization and grain growth .......................... 21  
1.4 Advantages of reversion treatment ................................. 23  
1.5 Aims of the study .................................................. 24  

2 **Experimental**  
2.1 Materials .................................................. 25  
2.2 Research methods and equipment ..................................... 25  

3 **Results**  
3.1 Microstructure and properties of cold-rolled steel ................. 27  
3.2 Microstructural evolution during annealing ....................... 28  
  3.2.1 Reversion of martensite ......................................... 28  
  3.2.2 Recrystallization of retained austenite ..................... 32  
  3.2.3 Austenite grain growth ........................................... 33  
3.3 Nucleation and growth of ε- and α’-martensite in tensile straining  
3.4 Mechanical properties ............................................ 38  
  3.4.1 Hardness evolution ............................................. 38  
  3.4.2 Tensile properties ............................................... 40  

4 **Discussion**  
4.1 Anisotropy of mechanical properties .............................. 43
| 4.2 ε- and α’-martensite transformation | 43 |
| 4.3 The impact of reversion and recrystallization on microstructure, grain size and grain growth | 45 |
| 4.4 Nucleation and growth of ε- and α’-martensite during plastic deformation | 47 |
| 4.5 Effect of microstructural evolution on mechanical properties | 48 |
| 4.6 Recommendations for further research | 52 |

5 Summary and conclusions 55
6 Novel features 57
List of references 59
Original publications 67
1 Introduction

1.1 Preface

For more than 60 years manganese has been considered a replacement for nickel in austenitic stainless steels, particularly at times of high nickel prices. Instead of adding nickel, these so-called “200-series” austenitic stainless steels are often alloyed with nitrogen and copper to stabilize the austenitic phase. As a result, a good combination of strength and ductility is provided. This enables the use of “200-series” austenitic stainless steels in a wide range of applications, with much lower alloying costs. [1,2]

Due to their good mechanical properties, formability and architectural image, typical applications for high-Mn steels are lightweight applications, such as indoor or outdoor architecture and bus bodies, as well as kitchenware, e.g., cutlery. In fact, in these applications high-Mn grades are designed to replace commonly used Cr-Ni austenitic grades (“300-series”). However, these steels are less resistant to corrosion than the “300-series”, which limits their applications. [1,2]

Austenitic stainless steels typically have good ductility and formability, but their yield strength is quite low. There are several methods for improving strength, e.g., solid solution strengthening, work hardening and grain size refinement. [3-5] Many “200-series” steels are metastable at room temperature, so that during cold working the formation of strain-induced martensite occurs readily, increasing strength. The disadvantage of strengthening by cold rolling is the formation of undesirable anisotropy in mechanical properties, with strength being different in different directions relative to the rolling direction. Therefore, other strengthening methods are desirable. [6]

Proper annealing treatment of cold-strengthened metastable austenitic stainless steel will revert strain-induced martensite back to austenite. Reverted austenite can have a fine grain size of a few hundred nanometers. As a result of this efficient grain size refinement, an excellent combination of yield strength and elongations is achievable, as shown in numerous studies during the last 25 years. [4,7-12]

However, the annealing cycle is a critical processing stage, as during prolonged or high-temperature annealing rapid grain growth tends to occur readily [3,4,9,13-15]. Therefore, prevention or retardation of grain growth becomes important. Fine precipitation is a method for used for this [16].
Alloying elements can be classified as either austenitic stabilizers, such as nickel, nitrogen, carbon, manganese, copper and cobalt, or ferrite stabilizers, such as chromium, silicon and molybdenum. Nickel addition is an effective way to ensure the austenitic structure of stainless steel. However, by adding other austenitic stabilizers, the austenitic structure can be achieved even without nickel, or with a low nickel content such as 1%. Nitrogen provides high-strength properties and copper improves drawability. When copper is added, nitrogen content can be reduced to obtain a softer material with better formability. Lowering nickel content without adding other austenite stabilizers, however, reduces the possible amount of chromium in the alloy, weakening corrosion resistance and narrowing the range of applications for which the steel is suited. [1,2,17]

Niobium is a ferrite stabilizer, but it is also a strong carbide- and nitride-forming element. Niobium carbides are much less soluble in austenite than, for instance, more unstable chromium carbide, and they form at relatively high temperatures [18]. In this way, niobium alloying helps refine grain size and retard recrystallization [19].

1.2 Plastic deformation of metastable austenitic stainless steels

Austenitic stainless steels have an fcc crystal structure due to the alloying. However, this structure is not thermodynamically stable at ambient temperatures. Therefore, applied stress or plastic deformation, e.g., cold rolling or tensile straining, may induce a martensitic phase transformation where the metastable austenite phase transforms into the thermodynamically more stable martensite phase, i.e., \( \gamma \rightarrow (\varepsilon) \rightarrow \alpha' \). Two different martensite phases may exist in austenitic stainless steels, hexagonal close-packed (hcp) \( \varepsilon \)-martensite and body-centred cubic (bcc) \( \alpha' \)-martensite. Due to the relatively low interstitial content, the crystal structure of \( \alpha' \)-martensite is normally referred to as bcc instead of bct (body-centred tetragonal).

1.2.1 Thermodynamics of strain-induced martensite transformation

The chemical free energy changes of the austenite and martensite phases as a function of temperature are illustrated schematically in Fig. 1. At temperature \( T_0 \) austenite and martensite are thermodynamically in equilibrium and at \( M_t \), martensitic transformation starts upon cooling. Martensitic transformation can occur only if the difference between the chemical free energies of the austenite and martensite phases reaches the critical value of \( \Delta \mathcal{G}_{M_t}^{\gamma-\alpha'} \). This takes place at
temperature $M_s$. However, the transformation can also occur at temperatures between $M_s$ and $T_0$ if a mechanical driving force $U'$ is applied. If $T_0$ is low enough, the microstructure remains austenitic. [20]

Fig. 1. Chemical free energy changes of the austenite and martensite phases according to Cahn and Haasen [20].

Fig. 2 shows that the critical applied stress to induce martensite formation increases linearly with an increase in stressing temperature in the range between $M_s$ and $M_d$. Below temperature $M_s$, yielding occurs by martensitic transformation, whereas at a higher temperature, by means of slip in the austenite phase. [20-21] According to Olson and Cohen [21], below temperature $M_s$, martensitic transformation is called stress-assisted and above it, strain-induced nucleation. The former occurs below the yield strength of the austenite phase with the aid of applied stress, and the latter occurs after plastic deformation of the austenite phase. Temperature $M_d$ is the upper limit for strain-induced transformation, as the chemical driving force of the phase transformation becomes so small that nucleation of martensite cannot be mechanically induced. [20,21] The characteristics of strain-induced martensite transformation can be modified by several factors, including chemical composition, temperature, strain rate, strain state and austenitising conditions [22].
1.2.2 Stacking faults, ε-martensite and deformation twinning

Stacking faults in austenite are formed between Shockley partial dislocations that form from the dissociation of a perfect dislocation. A stacking fault is a discontinuity in the stacking order of the \{111\} planes. Stacking fault energy (SFE) controls the width between two partial dislocations, since it balances the repulsive force between the partial dislocations. Austenitic stainless steels have low SFE, and therefore stacking faults are relatively wide, which makes cross-slip relatively difficult. SFE controls the formation of dislocation cells, twins and ε-martensite during plastic deformation. The lower the SFE of the steel, the lower the stability of austenitic stainless steel, and the higher the tendency for ε-martensite to form instead of twins [3,23-25].

A change in the sequence of the \{111\} plane produces a thin layer of a hexagonal close-packed phase. Hence, even a single stacking fault can be considered a nucleus of hcp ε-martensite [26]. The ε-martensite grows by an overlapping of stacking faults on every second \{111\} plane [27-29]. It is difficult to distinguish a single stacking fault, bundles of overlapping stacking faults, faulted and perfect ε-martensite, and therefore, the term “shear band” is often used to describe such microstructural features. [30]

Plastic deformation of austenitic stainless steel can induce deformation twinning. A deformation twin is formed as the result of gliding of Shockley partial dislocations of the same sign on successive adjacent \{111\} planes. Then the twin
grows in thickness. The driving force for twinning is the applied stress, while the driving force for martensite formation is the free energy difference between the austenite and martensitic phases, which may, however, be assisted by the applied stress. [3,31,32].

The incidence of ε-martensite, mechanical twins or dislocation glide are closely related to the SFE of the steel. ε-martensite formation is preferred when the chemical free energy difference between metastable austenite and ε-martensite phases is negative, as the hcp structure has lower energy than a twin with fcc stacking. An early work by Rémy and Pineau [24] on an Fe-Mn-Cr-C alloy suggested that ε-martensite transformation occurs when SFE is below ~13 mJ/m², twinning when SFE is between ~8 and ~40 mJ/m² and dislocation cells when SFE is above ~18 mJ/m². Later Allain et al. [33] studied an Fe-Mn-C system and Lee et al., [34] examined Fe-Cr-Mn-N-C alloys and concluded that strain-induced martensite transformation occurs if SFE is below 15 or 18 mJ/m² and formation of twins in steels if SFE is above 20 mJ/m², or between 12 and 35 mJ/m².

1.2.3 α'-martensite

α'-martensite has been found to nucleate on deformation-induced defects, such as shear bands [35,36] and their intersections [21,26,27,29,37-43], or at the intersection of deformation twins [29,43-47]. However, α'-martensite can also nucleate straight from austenite [48-52] and at grain boundaries [53-56]. As a shear band may consist of faulted and perfect ε-martensite, it is considered to be an intermediate phase in the formation of α'-martensite. [30,31,49,57]. Generally, α'-martensite nucleation involves a process by which an array of Shockley partial dislocations can penetrate through another shear band.

α'-martensite grows by repeated nucleation of new α'-martensite embryos and coalescence. At small strains, α'-martensite has been found to grow along slip planes, and with higher strains, outside of the active slip plane. Hence, the morphology is irregular and blocky. [43,58]

The γ → α' phase transformation affects the mechanical properties of metastable austenitic stainless steel. Firstly, it increases the strain hardening rate (SHR) and thereby increases tensile strength. For a metastable steel, a curve showing strain hardening as a function of increasing strain first exhibits a minimum and then a subsequent maximum [31,39,59-62]. Secondly, the strain hardening capability governs ductility, measured by uniform elongation. It has been shown that the rate and the point on the stress-strain curve at which α'-martensite
transformation takes place are important, rather than the total amount of formed $\alpha'$-martensite. The deformation temperature has a major impact on the microstructure formed, as austenite stability depends on temperature. With increasing temperature, $\alpha'$-martensite transformation is prevented. With decreasing temperature, $\alpha'$-martensite transformation and strain hardening occur readily at low strains, causing premature fracture. [60,63,64]

1.3 Reversion, recrystallization and grain growth

1.3.1 Reversion mechanism

$\alpha'$-martensite transformation into austenite ($\alpha' \rightarrow \gamma$) in ferrous alloys between the austenite start ($A_s$) and austenite finish ($A_f$) temperatures is known as reversion [65]. Two different reversion mechanisms are proposed in the literature: diffusion-type and shear-type mechanisms [7,8].

Diffusion-type reversion consists of random nucleation of austenite in $\alpha'$-martensite laths or at the lath boundaries. Austenite orientation in the crystallography is random. Then the nucleated grains grow into equiaxed grains. [8,10]

In the case of shear-type reversion, the $\alpha'$-martensite phase reverts back to the austenite phase via diffusionless transformation. The austenite formed contains a high dislocation density and its morphology is associated with the parent $\alpha'$-martensite. During prolonged annealing, defects recover to form sub-grains that then recrystallize into larger austenite grains in the range of a few $\mu$m [9]. Shear-type reversion occurs within a narrow temperature range of $\sim$50 °C, whereas diffusion-type reversion occurs over a larger temperature range of $\sim$200 °C [8,66,67]. Tomimura et al., [8] among others, studied 16Cr-10Ni and 18Cr-9Ni steels and found that at 10 s annealing reversion occurs through shear in a narrow temperature range of around 577 °C for the 16Cr-10Ni steel and through diffusion in a wider temperature range of 527–727 °C for the 18Cr-9Ni steel.

1.3.2 Factors affecting reversion

The reversion mechanism that is found to take place depends on the heating rate and chemical composition. A change in the reversion mechanism from diffusion-type to shear-type with an increasing heating rate has been reported in the literature.
by, e.g., Apple and Krauss, who studied Fe-Ni-C alloys with heating rates of 3 and 1500 °C/s [68], Montanari et al., who studied AISI 304 stainless steel with heating rates of 0.017–1.67 °C/s [69] and Leem et al., who found that the reversion mechanism in Fe-13Cr-7Ni-3Si martensitic stainless changed at 10 °C/s [70]. Moreover, the reversion mechanism can change from the shear-type, which occurs during heating, to the diffusion-type during subsequent isothermal holding [66].

Alloy composition affects the temperature dependence of the free energies of the \( \alpha' \) and \( \gamma \) phases. An increase in the Ni/Cr ratio causes an increase in the Gibbs free energy difference between \( \alpha' \) and \( \gamma \), leading to a change in the reversion mechanism from shear-type to diffusion-type. With decreasing \( T_0 \), the kinetics of diffusion required to transform \( \gamma \) to \( \alpha' \) by diffusion-type reversion decreases. The critical driving force for shear-type reversion is estimated to be about -500 J/mol. [8]

In an early work by Kaufman et al. [71], the free energy difference of the ternary Fe-Cr-Ni system was determined. Later, Somani et al. [9] further extended the equation to include the effects of other alloying elements, such as Si, Mn, Mo, C and N, which have a strong influence on the microstructure constitution, by adopting nickel and chromium equivalents instead of pure Ni and Cr. [72].

1.3.3 Recrystallization and grain growth

Austenite, which is deformed but not transformed during cold rolling, termed here as retained austenite (RA), can recrystallize during annealing. The driving force for recrystallization is the stored energy from the cold working. The new grains nucleate particularly at defects, such as shear bands and grain boundaries, and their growth consumes the whole RA structure. Recrystallization in austenitic stainless steels depends on several factors, such as cold rolling reduction, i.e., the amount of stored energy, initial grain size, alloy composition and annealing conditions, i.e., time, temperature and heating rate. [3,13,73]

In most studies concerning reversion annealing, e.g., [8,9,12], a mainly martensitic structure was used as a starting material for the annealing. In a partially martensitic structure, i.e., consisting of \( \alpha' \)-martensite and RA, the evolution of the microstructure is more complicated due to the slower kinetics of recrystallization compared with that of reversion [9,74-76]. However, only preliminary observations have been made concerning the competition between reversion and retained austenite.
After recrystallization, grain growth may occur with prolonged annealing. The driving force for grain growth is reduction of total grain boundary energy. At the atomic scale, this occurs by a net transfer of atoms from the concave side of curved grain boundaries to the convex side due to the lower free energy of the atoms on the convex side. Other things being equal, the greater the curvature of the boundary, the faster is its movement. Grain growth can be influenced e.g., by annealing temperature, solutes and particles. [3,13]

The kinetics of grain growth can be analysed using the generalized grain growth law, which can be written as:

\[ d^n - d_0^n = kt \]  

where \( d \) is average grain size, \( d_0 \) is initial grain size, \( n \) is the grain growth exponent, \( k \) is the kinetic parameter of grain growth and \( t \) is annealing time. In theory, \( n \) is equal to 2 for an ideal material, but for real materials \( n \) values are greater because grains are not spherical and there are chemical segregations. [3,77]. Therefore, higher values of \( n \), i.e., 2.4–10, have been reported in the literature for austenitic stainless steels and nanocrystalline materials [78,79].

The kinetic parameter \( k \) can be used to estimate the activation energy for the grain growth process, which can be written as follows:

\[ k = k_0 e^{\left(\frac{\Delta G_{activation}}{RT}\right)} \]  

where \( k_0 \) is a material constant, \( \Delta G_{activation} \) is the activation energy for grain growth, \( R \) is a gas constant and \( T \) is annealing temperature. [3] Activation energies of grain growth between 280–455 kJ/mol have been reported in the literature for austenitic stainless steels [79-81].

Grain size is controlled by competition between the driving force for grain growth and the pinning force, so that if the pinning force exceeds the driving force, the boundary will be pinned, i.e., immobile. There are models for describing the driving force for grain growth, and Zener described it as follows:

\[ F_d = \frac{2\gamma}{D} \]  

where \( F_d \) is the driving force predicted by Zener, \( \gamma \) is grain boundary energy and \( D \) is the average radius of the sphere. [82]

Second-phase particles exert a pinning force on grain boundaries and they can inhibit grain growth. The pinning pressure depends on the size, volume fraction and distribution of the particles. At high annealing temperatures, second-phase particles can form, coarsen or dissolve. [3,13]
There are various models for explaining how precipitates can suppress austenite grain growth by pinning grain boundaries. The flexible boundary model (FBM) assumes that an infinitely flexible boundary is capable of interacting with every particle in a three-dimensional array until it is fully pinned. It can be expressed as follows:

\[ F_p = \frac{3f^{2/3}r}{\pi r} \]  

where \( F_p \) is the pinning force according to the flexible boundary model, \( f \) is the volume fraction of the particles and \( r \) is the radius of the spherical particles.

1.4 Advantages of reversion treatment

Generally, improved mechanical properties can be obtained in metastable austenitic stainless steels subjected to reversion annealing, since the reversion treatment refines grain size, e.g., [4,8,9,12,72]. During cold forming, \( \varepsilon \)- and \( \alpha' \)-martensite form from the metastable austenitic structure, and \( \alpha' \)-martensite grows by repeated nucleation of the embryos and their coalescence. The fraction of \( \alpha' \)-martensite increases with increasing straining. In diffusional reversion, austenite nucleates at martensite laths or grain boundaries of \( \alpha' \)-martensite, and generally there are a large number of nucleation sites for austenite inside \( \alpha' \)-martensite. Hence, the final grain size will be much finer than before the treatment. In the instance of shear reversion, the reverted austenite inherits the martensitic grain structure with a high dislocation density. The reversion is followed by recrystallization, leading to a refined grain size. [8,43,58,67,84]

A highly refined grain size of 0.54 \( \mu \text{m} \) has been reported for commercial 301LN austenitic stainless steel, giving a superior combination of yield strength and uniform elongation: 700 MPa and 35%, respectively [4]. However, precipitation of \((\text{Fe,Cr,Mo})_2\text{C_6}\) carbides and CrN and Cr\(_2\)N nitrides may occur at reversion annealing temperatures, which can have a detrimental effect on corrosion properties [4,84,85].

Grain size strengthening can be described with the Hall-Petch equation, which can be written as follows:

\[ \sigma_y = \sigma_0 + kd^{-1/2} \]  

where \( \sigma_y \) is yield strength, \( \sigma_0 \) is yield strength without the contribution of grain boundaries, \( k \) is a constant, and \( d \) is average grain size. Yield stress increases with
decreasing grain size, as pile-ups in fine-grained materials contain fewer dislocations and the stress at the tip of the pile-up decreases. Therefore, a larger applied stress is required to generate dislocations in adjacent grains. Overall, the strengthening effect in austenitic stainless steels is due to various strengthening mechanisms, such as solid solution strengthening, precipitate strengthening, strain hardening and grain boundary strengthening, all of which are dependent on annealing temperature. [4,13]

1.5 Aims of the study

The objective of this thesis work was to study the relationships between processing and achieved properties of high-manganese low-nickel austenitic stainless steel. The steel was chosen due to its metastable characteristics. Austenitic stainless steels have potential for further optimization of mechanical properties through adjustment of the deformation mechanisms in cold working and control of subsequent treatments, such as reversion and recrystallization annealing. The objectives of this work can be divided into the following tasks:

- To study the details of the transformation of martensite and its reversion.
- To characterize various microstructures, i.e., reverted, retained and recovered austenite and their combinations, achieved via reversion annealing.
- To study the potential of reversion treatment to improve mechanical properties and to understand the influence of the various microstructures formed during reversion annealing on the mechanical properties of low-nickel austenitic stainless steels.
- To investigate if reversion annealing can eliminate anisotropy at a high strength level.
- To reveal how the grain size distribution of reverted ultrafine-grained austenite and coarse cold-worked austenite affects strain-induced martensite formation, strength and ductility during tensile testing.
- To study the influence of microalloying on microstructures and mechanical properties, and to clarify the ways in which microalloying affects reversion and recrystallization kinetics, grain size refinement and the mechanical properties achieved.
- To establish the potential of microalloying to widen the processing window for reversion heat treatment of the steel concerned.
2 Experimental

2.1 Materials

The steel used as experimental material was “200-series” austenitic stainless steel, 15Cr-9Mn-1Ni-2Cu (204Cu steel; coded as 0Nb). It was a cold-rolled and annealed final product in 2B delivery condition from Outokumpu Stainless Oy (Tornio, Finland) production and it was cold-rolled to 5, 12 or 20% thickness reduction in a laboratory rolling mill in order to study of the influence of light cold rolling reductions on the anisotropy of the mechanical properties of the steel. Reduction of 60% was taken as the highest practical cold rolling reduction on a production line. To investigate the influence of alloying, four 60-kg charges of pure raw materials, alloyed with various contents of Nb, were melted in a laboratory vacuum induction furnace. Cast ingots were machined, subsequently heat-treated at 1265 °C for 60 min, hot-rolled with 9 passes to a final thickness of 4 mm, annealed at 1100 °C for 5 min, water quenched and pickled and cold-rolled to a final thickness of 1.5 mm (corresponding to ~60% thickness reduction) at the Tornio Research Center. The materials were coded, based on their Nb content, as 0.05Nb, 0.11Nb, 0.28Nb and 0.45Nb. The final thicknesses were 0.4 mm for the 0Nb and 1.5 mm for the Nb-alloyed sheets. The chemical compositions of the steels are listed in Table 1.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>N</th>
<th>Nb</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0Nb</td>
<td>0.079</td>
<td>0.40</td>
<td>9.00</td>
<td>15.2</td>
<td>1.1</td>
<td>1.68</td>
<td>0.115</td>
<td>-</td>
<td>bal.</td>
</tr>
<tr>
<td>0.05Nb</td>
<td>0.070</td>
<td>0.30</td>
<td>9.13</td>
<td>15.2</td>
<td>1.1</td>
<td>1.70</td>
<td>0.165</td>
<td>0.05</td>
<td>bal.</td>
</tr>
<tr>
<td>0.11Nb</td>
<td>0.072</td>
<td>0.28</td>
<td>9.19</td>
<td>15.2</td>
<td>1.1</td>
<td>1.74</td>
<td>0.130</td>
<td>0.11</td>
<td>bal.</td>
</tr>
<tr>
<td>0.28Nb</td>
<td>0.083</td>
<td>0.28</td>
<td>9.19</td>
<td>15.1</td>
<td>1.1</td>
<td>1.74</td>
<td>0.160</td>
<td>0.28</td>
<td>bal.</td>
</tr>
<tr>
<td>0.45Nb</td>
<td>0.100</td>
<td>0.30</td>
<td>8.90</td>
<td>15.2</td>
<td>1.1</td>
<td>1.70</td>
<td>0.160</td>
<td>0.45</td>
<td>bal.</td>
</tr>
</tbody>
</table>

2.2 Research methods and equipment

The cold-rolled samples were annealed at the University of Oulu using a Gleeble 1500 or Gleeble 3800 thermo-mechanical simulator. The heating rate was 5 °C/s for annealing tests performed at 450, 500, 550, 585 and 620 °C for 0.1, 1, 10, 100, 300 and 600 s, 50 °C/s, 150 °C/s or 200 °C/s for annealing tests performed at 700, 800, 900, 1000 and 1100 °C for 0.1, 1, 10, 100, 200, 500 and 1000 s. In every test the cooling rate was 200 °C/s down to 400 °C, followed by free cooling.
A Feritscope ® (Helmut Fisher FMP 30) instrument was used to quantify the ferromagnetic $\alpha'$-martensite in the steel. The readings of the instrument were multiplied by a correction factor of 1.7 [86]. X-ray diffraction (XRD) (Siemens-D500) was used to determine the volume fraction of $\varepsilon$-martensite at the cold-rolled stage and to estimate the dislocation density of $\alpha'$-martensite.

Microstructural examinations were performed using a light optical microscope (LOM) (Nikon Eclipse MA100), field emission scanning electron microscopes together with electron backscatter diffractions units (EBSD) (Zeiss Ultra Plus FEG-SEM with a HKL EBSD detector and Zeiss Sigma FEG-SEM with an EDAX EBSD detector) and transmission electron microscopes (TEM) (LEO 912 FETEM and Hitachi H7600 TEM).

Mechanical properties were determined at room temperature using tensile testing (Zwick / Z100) at strain rates of $7.5 \times 10^{-4}$ s$^{-1}$ up to 2% strain (0.2% proof stress) after which the strain rate was $5 \times 10^{-3}$ s$^{-1}$ for cold-rolled specimens and $5 \times 10^{-4}$ s$^{-1}$ for reversion-treated specimens. Because of the limitations of the size of the uniformly heated zone in the Gleeble specimens, the tensile test specimens had a non-standard specimen geometry with a short 15 mm long gage length [87]. The hardness of the specimens was determined with micro-hardness measurements (CSM Instrument, micro-indentation tester) with a 10 mg load and a Berkovich indenter.

Table 2 presents the test materials and the equipment and methods for microstructure characterization employed in Papers I–VI.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Steel</th>
<th>Microstructure characterization equipment and method</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0Nb</td>
<td>Feritscope, LOM, Zeiss Ultra Plus FEG-SEM + HKL EBSD detector, tensile testing, micro-indentation tester</td>
</tr>
<tr>
<td>II</td>
<td>0Nb</td>
<td>Feritscope, LOM, Zeiss Ultra Plus FEG-SEM + HKL EBSD detector, LEO 912 FETEM, tensile testing</td>
</tr>
<tr>
<td>III</td>
<td>0Nb</td>
<td>Feritscope, XRD, Hitachi H7600 TEM, micro-indentation tester</td>
</tr>
<tr>
<td>IV</td>
<td>0Nb, 11Nb, 0.45Nb</td>
<td>Feritscope, XRD, LOM, Zeiss Sigma FEG-SEM + EDAX EBSD detector, micro-indentation tester</td>
</tr>
<tr>
<td>V</td>
<td>0Nb, 0.05Nb, 0.11Nb, 0.28Nb, 0.45Nb</td>
<td>Feritscope, LOM, Zeiss Sigma FEG-SEM + EDAX EBSD detector, LEO 912 FETEM</td>
</tr>
<tr>
<td>VI</td>
<td>0Nb</td>
<td>Feritscope, LOM, Zeiss Ultra Plus FEG-SEM + HKL EBSD detector, Hitachi H7600 TEM, tensile testing</td>
</tr>
</tbody>
</table>
3 Results

3.1 Microstructure and properties of cold-rolled steel

Initially, the 0Nb steel was fully austenitic without any α'-martensite, (Papers I–VI). After 5, 12 or 20% cold rolling reduction, the α'-martensite fractions were 2, 10 and 24% (Paper II). After 60% cold rolling reduction, the α'-martensite fractions of the 0Nb steel were 33% (Papers I and II) or 60% (Papers III–VI). This indicates a high sensitivity towards α'-martensite formation during cold rolling. The α'-martensite fractions of the 0.05Nb, 0.11Nb, 0.28Nb and 0.45Nb steels were 53, 63, 47 and 49%, respectively (Papers IV and V). No ε-martensite was detected in the steels after 60% cold rolling (Paper IV).

The microstructures of the 0Nb steel after various cold rolling reductions are shown in Fig. 3. At low reductions, slip bands containing ε/α'-martensite and wide stacking faults become visible (Fig. 3a,b). With increasing rolling reduction, the number of slip bands increased and finally α'-martensite covered several grains (Fig. 3c–e).

The anisotropy of the tensile properties of the 0Nb steel caused by cold rolling was analysed in Paper II. Yield strengths (Rp0.2 = 0.2% proof stress) in the longitudinal
direction and the transverse direction after 5, 12, 20 and 60% cold rolling are shown in Table 3. It is seen that yield strength increased with rolling reduction and the values were higher in the transverse direction than in the longitudinal direction. Anisotropy appeared already at 5% reduction, and anisotropy seemed to be the smallest with 60% reduction.

Table 3. Yield strengths (R_p0.2) of the 0Nb steel after 5, 12, 20 and 60% cold rolling reductions in the longitudinal (LD) and transverse directions (TD). [Paper II, Published by permission of AIM Editorial Office]

<table>
<thead>
<tr>
<th>Cold rolling reduction [%]</th>
<th>5</th>
<th>12</th>
<th>20</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_p0.2 LD</td>
<td>583</td>
<td>692</td>
<td>815</td>
<td>1522</td>
</tr>
<tr>
<td>R_p0.2 TD</td>
<td>632</td>
<td>740</td>
<td>881</td>
<td>1544</td>
</tr>
</tbody>
</table>

3.2 Microstructural evolution during annealing

In reversion annealing, the steel sheet is heated at a certain rate to the final annealing temperature. Depending on the heating rate and soaking temperature, during either this heating stage or soaking, α’-martensite will revert back to austenite. Reversion occurs by either shearing or diffusion. At a higher temperature than required for reversion, cold-deformed retained austenite recrystallizes and reverted grains grow. During high-temperature annealing, i.e., 1000–1100 °C, grain growth occurs. The microstructural evolution during reversion and recrystallization annealing is discussed in detail in the following sections.

3.2.1 Reversion of martensite

α’-martensite transformation to austenite in the 0Nb steel was studied in Paper III. Fig. 4 shows the relative change in the specimen’s width (Fig. 4a) and its first derivative (Fig. 4b) as a function of heating temperature. In the course of continuous heating, in addition to the approximately linear thermal expansion of the austenite-martensite structure, the width increased more rapidly in the temperature range of 550–700 °C, indicating formation of athermal martensite. Then the width decreased, indicating phase transformation, and finally expanded approximately linearly as the structure became austenitic. Fig. 4b shows that the peaks in the curves shifted to higher temperatures with the increasing heating rate.
Fig. 4. a) Relative change in width ($\Delta W/W_0$) and b) its first derivate ($d(\Delta W/W_0)dT$) as a function of heating temperature at heating rates of 5–150 °C/s for the 0Nb steel. [Paper III, Published by permission of Trans Tech Publications Inc.]

Fig. 5a shows the formation of new martensite, i.e., athermal martensite, during heating to 620 °C for 0.1 s. Compared with the value prior to heating, there is about 12% units more $\alpha'$-martensite. In view of the above results, it was considered interesting to study whether $\alpha'$-martensite would continue to form during isothermal holding after heating. Isothermal martensite was found to form after heating, e.g., at 550 °C for 100 s. No $\alpha'$-martensite was detected after annealing at 1100 °C for 1000 s and cooling, suggesting that no $\alpha'$-martensite is formed during cooling to room temperature.

Fig. 5b displays a TEM image of $\alpha'$-martensite present after annealing at 550 °C for 100 s, revealing that the $\alpha'$-martensite presented before heating has already tempered. To find out the changes in the dislocation density of $\alpha'$-martensite, XRD spectra were subjected to Rietveld analyses using the MAUD program [88]. The dislocation density of $\alpha'$-martensite after 60% cold rolling was found to be $5.04 \times 10^{15}$ m$^{-2}$. During heating to 620 °C and quenching, i.e., 0.1 s annealing, the dislocation density was decreased to $1.55 \times 10^{15}$ m$^{-2}$, even though reversion did not yet occur. After 10, 100 and 300 s soaking at 550 °C, the dislocation densities were 2.52, 1.41 and 1.03 $\times 10^{15}$ m$^{-2}$. Hence, the overall dislocation density of the samples (containing old and newly formed martensite) decreased over the course of soaking even at this low temperature, i.e., tempering of $\alpha'$-martensite took place.
Fig. 5. Development of fraction and structure of α'-martensite in the 0Nb steel. a) the volume fraction of α'-martensite after annealing at various temperatures for various times and b) TEM micrograph of the specimen after annealing at 550 °C for 100 s. [Paper III, Published by permission of Trans Tech Publications Inc.]

Fig. 4b shows that the reversion starting and finishing temperatures during continuous heating depend on the heating rate. The reversion kinetics of α'-martensite to austenite during isothermal annealing was investigated in Papers I–VI. The α'-martensite fractions measured after heating to 700 °C at 200 °C/s and holding for various annealing times are plotted in Fig. 6, which also includes data for the Nb-alloyed steels (Papers IV and V). According to the figure, reversion of the 0Nb steel is fast, but it is apparent that Nb alloying retards reversion. At 800 °C all the α'-martensite reverted back to austenite within 1 s (Papers I, II and VI).

Fig. 6. α'-martensite fractions of the 0–0.45Nb steels after heating at 200 °C/s to 700 °C and holding for various durations. [Paper V, published by permission of The Iron and Steel Institute of Japan]

Fig. 7 shows the microstructural evolution during annealing at 700 °C for various times. The microstructure of the 0Nb steel after 10 s was non-uniform, consisting of ultrafine reverted austenite grains and large RA grains (Fig. 7a). Within 100 s of
annealing, all the $\alpha'$-martensite was reverted back to austenite (Fig. 7b), but it took a long time before RA started to recrystallize, with recrystallization being incomplete after 1000 s (Fig. 7c).

Evidence of both shear-type and diffusion-type reversion mechanisms was observed, as shown in Figs. 6–7. The reversion was fast, being completed within 10 s in the 0Nb steel and within 100 s in the Nb-alloyed steels (Fig. 6). The EBSD image quality was low in some areas (examples marked as Shear rev. in Fig. 7a,d) and new fine grains could hardly be seen after 1000 s, as typical features of shear-type reversion. However, large areas consisting of new, fine, equiaxed grains were also visible (examples marked as Diff. rev. in Fig. 7a,d), as typical features of diffusion-type reversion. Recrystallization was slower in the Nb-alloyed steels, so that even after 1000 s of soaking, no traces of recrystallized RA grains were seen yet (Fig. 7e,f).

Fig. 7. Inverse pole figure (a,d) and LOM (b,c,e,f) images after cold rolling and annealing at 700 °C for the 0Nb (a–c), 0.11Nb (d,e) and 0.45Nb (f) steels for a,d) 10 s, b) 100 s and c,e,f) 1000 s. [Paper IV, published by permission of Elsevier Ltd.]

An example of TEM examinations of the 0Nb steel showed nucleation of new, dislocation-free and equiaxed austenite grains at the lath boundaries of the $\alpha'$-
martensite phase when annealed at 700 °C for 100 s, Fig. 8a. The size of reverted austenite was 300–400 nm, as presented in Fig. 8b.

![Microstructure of the 0Nb steel after annealing at 700 °C for 100 s, showing a) nucleation of austenite from α'-martensite and b) a reverted equiaxed austenite structure.](image)

**3.2.2 Recrystallization of retained austenite**

Recrystallization of RA required higher temperatures than reversion, as seen in Fig. 9, Papers I, II, IV and V. Nucleation of recrystallization in RA grains tended to occur at 800 °C, starting at shear bands crossing RA grains, their intersections and grain boundaries (see white circles in Fig. 9).

![Inverse pole figure images after annealing at 800 °C for 10 s for the a) 0Nb, b) 0.11Nb and c) 0.45Nb steels.](image)

Reversion was completed within 1 s at 800 °C, but RA recrystallized later during 1000 s of annealing. The occurrence of two processes at this temperature, i.e.,
reversion and recrystallization, resulted in a non-uniform grain size distribution, as seen in Fig. 10 (Paper IV). In Fig. 10a, fine, reverted areas are shown in red and coarser recrystallized RA areas in blue. The bimodal grain size distribution was due to the fact that ultrafine grains are formed from the reverted $\alpha'$-martensite and larger grains from RA (Fig. 10b). After annealing at 800 °C for 1000 s, the average grain sizes were 1.7, 1.1 and 1.0 $\mu$m for the 0Nb, 0.11Nb and 0.45Nb steels, respectively.

![Fig. 10. a) Image quality map and b) grain size distribution (taken from the coloured areas) of the 0Nb steel after annealing at 800 °C for 1000 s. [Paper IV, published by permission of Elsevier Ltd.]](image)

### 3.2.3 Austenite grain growth

To obtain a uniform austenite grain size, an annealing temperature of 900 °C or higher is preferred, as demonstrated in Papers I, II, IV and V. Fig. 11a–c shows an example, determined using EBSD, of the uniform grain structure of the 0Nb, 0.11Nb and 0.45Nb steels, with average grain sizes of 1.9, 1.4 and 1.4 $\mu$m, respectively. These grain sizes are fine, but significant grain coarsening occurred during annealing at 1100 °C for 1000 s, as evident in Fig. 11d–f.
The efficiency of Nb alloying in retarding grain growth was investigated in paper V. Various grain sizes are achievable via reversion treatments, for instance 2–9 μm after annealing at 900–1100 °C for 1 s, as shown in Fig. 12, and in Papers I and V. Grain size naturally increased with increasing temperature or time, but decreased with increasing Nb content due to retardation of grain coarsening by Nb. According to Fig. 12, the concentration of 0.11 wt.% Nb was high enough to inhibit grain growth at 900 and 1000 °C (Fig. 12a,b), but a higher Nb content of 0.28 wt.% was needed to have an effect at 1100 °C (Fig. 12c). Despite some grain growth, reversion can be seen to be an effective way to refine grain size, as the initial grain size of the 0Nb steel before cold rolling was 18 μm.

The kinetics of grain growth can be estimated using the measured grain sizes, annealing durations and the grain growth equation (Equation 1). Further, the calculated kinetic parameter can be applied to determine the activation energy for grain growth (Equation 2). Based on the experimental data, the activation energies for grain growth in the 0Nb, 0.11Nb and 0.45Nb steels were calculated to be 363, 373 and 458 kJ/mol, respectively.
Grain size is controlled by competition between the driving force ($F_d$) (Equation 3) and pinning force ($F_p$) (Equation 4) for grain growth. If the pinning force exceeds the driving force, the boundary will be pinned and no grain growth occurs. The volume fraction of precipitates was estimated from TEM replicas, Paper V. As an example, Fig. 13 presents typical TEM images of the precipitation structure of the 0.45Nb steel after annealing at 1100 °C for 1 s (Fig. 13a) and 1000 s (Fig. 13b). The results of the calculations using Equations 3 and 4 after annealing at 1100 °C for 1 and 1000 s are shown in Fig. 14. It seems that 0.28 wt.% Nb was efficient in retarding grain coarsening after annealing at 1100 °C, as also observed in grain size measurements.
3.3 Nucleation and growth of $\varepsilon$- and $\alpha'$-martensite in tensile straining

To clarify the influence of refined grain size on strain-induced martensite transformation in tensile straining, the formation of $\varepsilon$- and $\alpha'$-martensite during straining in various structures, i.e., ultrafine grains (UFG, average grain size 0.5 $\mu$m) and retained austenite (RA), micron-scale grains (MG, average grain size 1.5 $\mu$m) and RA, fine grains (FG, average grain size 4 $\mu$m) and coarse grains (CG, average grain size 18 $\mu$m), was investigated using EBSD in Paper VI. The structures were obtained by various reversion treatments and $\alpha'$-martensite
fractions were determined as a function of straining by interrupting the tensile test for the measurement, Fig. 15.

Fig. 15. α’-martensite contents in different structures as a function of tensile strain for the 0Nb steel. [Paper VI, published by permission of Elsevier Ltd.]

In UFG, no ε-martensite was detected at any stage of deformation, but in MG, FG and CG, traces of ε-martensite were found after 10% (Fig. 16a) and 20% (Fig. 16b) strain. In RA grains, ε-martensite appeared already after 2% strain and was found even after 20% strain (Fig. 16c). α’-martensite formed along shear bands even after 2% of straining in the UFG-RA structure and later in the MG-RA structure.

In UFG, TEM examinations revealed numerous stacking faults (Fig. 16d) and thin mechanical twins (Fig. 16e) already after 2% strain. After 20% strain, austenite grains seemed heavily deformed, with shear bands covering the grains (Fig. 16f).

In MG, extended dislocations in one or two slip systems and mechanical twins were seen after 2% strain (Fig. 16g). At 10% strain, ε- and α’-martensite were formed in the coarser austenite grains, while shear bands crossed some finer grains entirely (Fig. 16h).

After 2% strain, extended dislocations and stacking faults were seen in the FG and CG microstructures (Fig. 16i). After 10% strain in FG, shear bands appeared in one slip system, and in two slip system in CG (Fig. 16a). Both ε- and α’-martensite were detected at shear bands in the both structures, but only α’-martensite at austenite grain boundaries. The α’-martensite nucleated and grew at the intersection of two ε-martensite laths, shear bands and along austenite grain boundaries, and sometimes via ε-martensite. Hence, the types of nucleation sites changed with grain size refinement.
Fig. 16. EBSD (a–c) and TEM (d–i) images of various structures with average grain size (GS) after 2, 10 or 20% straining for the 0Nb steel. [Paper VI, published by permission of Elsevier Ltd.]

3.4 Mechanical properties

3.4.1 Hardness evolution

To improve our understanding of the occurrence of the reversion and recrystallization processes required for grain refinement, the softening of the $\alpha'$-martensite, reverted grains and RA grains during the course of annealing was investigated using microhardness (HV0.01) measurements, Fig. 17, Papers I and IV. After 60% cold rolling, the microhardness of $\alpha'$-martensite was 665, 746 and
777 HV and that of RA grains 626, 622 and 629 HV for the 0Nb, 0.11Nb and 0.45Nb steels, respectively. The hardness of α’-martensite decreased gradually in the beginning of the annealing process, obviously due to tempering, Fig. 17a. As shown earlier in Section 3.2.1, pronounced tempering of α’-martensite occurred already in the heating stage, seen similarly here corresponding to 0.1 s time. At 700 °C, the hardness of reverted grains dropped with continuing annealing time, especially in the 0Nb steel, where there were no precipitates to hinder the decrease in dislocation density of shear-reverted grains or the grain coarsening of diffusion-reverted ultrafine grains. At 700 °C, the hardness of RA grains decreased slowly in the beginning of the annealing process, Fig. 17b. However, after 100 s, the hardness of the 0Nb steel dropped, revealing the start of static recrystallization. A similar drop did not happen in the Nb-alloyed steels, indicating the retarding effect of Nb alloying on recrystallization kinetics.

At 800 °C, the hardness of reverted grains decreased slowly due to grain growth, Fig. 17c. In RA grains, the hardness in the 0Nb steel dropped after 10 s of annealing, and later in the 0.11Nb and 0.45Nb steels, after 40 and 60 s, Fig. 17d. The data clearly show the retarding effect of Nb alloying on the start of static recrystallization. Based on the hardness behaviour, it seems that recrystallization became completed within 20 s in the 0Nb steel, whereas only within 200 s in the 0.45Nb steel. Hence, recrystallization took place distinctly slower than reversion, especially in the Nb-alloyed steels.
3.4.2 Tensile properties

To understand the dependence of mechanical properties on microstructure, the mechanical properties of the reversion-treated steels were determined using tensile tests. The strength and ductility properties were investigated in Papers I, II, IV and VI. Fig. 18 shows that anisotropy in mechanical properties present after cold rolling practically disappeared as the grain structure became reverted and recrystallized.
Fig. 18. Anisotropy of yield strength in the reversion-treated 0Nb steel containing $\alpha'$-martensite, reverted austenite (Rev.), RA and recrystallized austenite (Rex.). LO = longitudinal direction, TR = transverse direction. [Paper II, Published by permission of AIM Editorial Office]

Fig. 19 illustrates the true stress-true strain and strain hardening behaviour of the steels annealed at 700, 800 and 900 °C for various durations. It is seen that after annealing at 700 °C for 10 s (Fig. 19a), i.e., the microstructure consisting of $\alpha'$-martensite, reverted and RA, yield strength was in the range of 1060–1140 MPa, increasing with Nb content, while uniform elongations ($A_u$) was 38–42%. Annealing at 700 °C for a longer time, 1000 s (Fig. 19b), which resulted in reverted fine-grained austenite and recovered and partially recrystallized RA, caused yield strength to decrease significantly. Annealing at 800 °C for 10 s (Fig. 19c), i.e., the similar reverted and recovered, and partially recrystallized retained austenitic microstructure as above, provided lower yield strength similarly as the uniform austenitic grain structure obtained at 900 °C for 10 s (Fig. 19d). Table 4 compares the mechanical properties achieved and average grain size (measured using EBSD), excluding RA of the studied steels.

For all the steels, strain hardening exhibited two-stage hardening behaviour, with small strains the strain hardening rate (SHR) dropped steeply, reaching a minimum at small strains, and then increased to a peak at higher strains before finally declining.
Fig. 19. Strain hardening rate and true stress as a function of true strain for the 0Nb, 0.11Nb and 0.45Nb steels after annealing at a) 700 °C for 10 s, b) 700 °C for 1000 s, c) 800 °C for 10 s and d) 900 °C for 10 s. [Paper IV, published by permission of Elsevier Ltd.]

Table 4. Mechanical properties (Rp0.2, Rm and Ag) and grain size (GS) of the 0Nb, 0.11Nb and 0.45Nb steels. The α’-martensite fraction formed during cold rolling is marked as α’ and reversion annealing treatment (annealing temperature – time) as Ann. Some steels also include RA, marked as *. [Papers IV and VI, Published by permission of Elsevier Ltd.]

<table>
<thead>
<tr>
<th>Steel</th>
<th>α’ [%]</th>
<th>Ann. [°C – s]</th>
<th>Rp0.2 [MPa]</th>
<th>Rm [MPa]</th>
<th>Ag [%]</th>
<th>GS [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0Nb</td>
<td>60</td>
<td>700 – 10</td>
<td>1185</td>
<td>1308</td>
<td>43</td>
<td>0.5*</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>700 – 100</td>
<td>899</td>
<td>1345</td>
<td>38</td>
<td>0.5*</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>700 – 1000</td>
<td>605</td>
<td>1180</td>
<td>36</td>
<td>0.8*</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>800 – 10</td>
<td>542</td>
<td>1067</td>
<td>63</td>
<td>0.6*</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>900 – 10</td>
<td>441</td>
<td>1049</td>
<td>59</td>
<td>1.9</td>
</tr>
<tr>
<td>0.11Nb</td>
<td>63</td>
<td>800 – 10</td>
<td>813</td>
<td>1117</td>
<td>51</td>
<td>0.6*</td>
</tr>
<tr>
<td></td>
<td>900 – 10</td>
<td>564</td>
<td>1005</td>
<td>59</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>0.45Nb</td>
<td>49</td>
<td>800 – 10</td>
<td>778</td>
<td>1105</td>
<td>52</td>
<td>0.6*</td>
</tr>
<tr>
<td></td>
<td>900 – 10</td>
<td>575</td>
<td>1031</td>
<td>63</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>
4 Discussion

4.1 Anisotropy of mechanical properties

The disadvantage of strengthening by cold rolling is the formation of harmful anisotropy in mechanical properties, which limits applications. Reversion annealing and grain size refinement is an alternative strengthening method that causes less anisotropy in mechanical properties.

In temper rolling of the 0Nb steel, directional anisotropy in yield strength was already present at such a low thickness reduction as 5%, similarly as also previously observed for austenitic 301LN stainless steel [6,87]. At this stage, only 2% $\alpha'$-martensite is formed in the steel. Hence, $\alpha'$-martensite cannot be a major reason for the anisotropy. It has been suggested that anisotropy in mechanical properties at light reductions results from a dislocation structure formed in the austenite, i.e., numerous stacking faults, slip activity in two systems (Fig. 3), twinning (Fig. 16) and texture, i.e., a mixture of copper, brass and Goss components [89-92].

After reversion treatment, the anisotropy in mechanical properties disappeared in the structure containing annealed soft grains with low dislocation density, as also observed by Miettunen [87]. Slight anisotropy was still left in partially softened structures (Fig. 18), indicating that the anisotropy is related to the dislocation structure of deformed austenite. It has been observed in 301LN steel [9] that the texture of reverted fine-grained austenite is strong compared with the typical texture of commercially cold-rolled and annealed steel, dominated by strong Brass and Goss orientations and minor Copper and S orientations. Hence, we can notice that this texture does not seem to be a factor affecting anisotropy. Because almost full reversion and recrystallization was required to completely eliminate the anisotropy, maximal strength cannot be utilized; however, grain size after complete reversion treatment is more than one order of magnitude finer than that of the initial structure, providing a relatively high yield strength, about 600 MPa.

4.2 $\varepsilon$- and $\alpha'$-martensite transformation

The formation $\varepsilon$- and $\alpha'$-martensite during tensile testing and cold rolling was followed in order to understand the microstructures formed in reversion annealing. In the 0Nb steel, after 2–20% tensile straining some $\varepsilon$-martensite formed in structures consisting of grains larger than 4 $\mu$m (Paper VI), but after 60% cold
rolling no ε-martensite was detected in XRD measurements (Paper IV). This clearly indicates that ε-martensite is an intermediate phase in α'-martensite nucleation, as also shown previously, e.g., [27,34,41,43,57]. The dislocation density of the cold-rolled 0Nb steel was high, 5.04 x 15 m⁻², which is consistent with the values reported in the literature for austenitic stainless steels, such as 304 and 301LN [62,93]. However, the stability of the studied steels was rather high. Therefore, the 60% cold rolling did not result in complete transformation to α'-martensite. In the partially transformed structure, α'-martensite reversion can only refine part of the structure and recrystallization is required for grain size refinement of the cold-rolled RA.

During heating of 17Mn-0.06C TRIP/TWIP steel, ε-martensite has been found to revert to austenite in the very beginning of the annealing process, over a temperature range of 100–250 °C [94]. However, upon heating the 0Nb steel without ε-martensite at the heating rate of 5–150 °C/s, the specimen’s width increased around the temperature of 550–700 °C (Fig. 4, Paper III), depending on the heating rate. The formation of athermal bcc-martensite from fcc-austenite resulted in this volume expansion, as confirmed by α'-martensite measurements, Fig. 5. However, dislocation density measurements only showed a decrease in the dislocation density compared with the cold-rolled state, due to the tempering of old α'-martensite. As the volume fraction of initial α'-martensite was higher than the fraction of athermally formed new martensite, the overall dislocation density of the specimen decreased.

During heating at a rate of 5–150 °C/s, reversion occurred over the temperature range 600–800 °C and was seen as a decrease in the width of the specimen. In addition to athermal martensite formation during continuous heating, new martensite formed isothermally during annealing at a constant temperature, e.g., at 550 °C for 300 s, Fig. 5. The overall dislocation density of the specimen annealed at 550 °C for 300 s decreased due to the tempering of α'-martensite and relaxation of microstresses at the γ/α' interfaces, enabling the growth of new martensite (Paper III) [73,95]. Another proposed mechanism for the formation of new martensite in annealing is the formation of precipitates that deplete the matrix from austenite stabilizer elements, allowing the Ms temperature to increase locally [9,73,76,95]. However, no evidence of precipitates was seen in the microstructure (Fig. 5b).
4.3 The impact of reversion and recrystallization on microstructure, grain size and grain growth

Reversion and recrystallization of RA during annealing were investigated in Papers I–V. Upon annealing at a temperature of 700 °C, $\alpha'$-martensite reverted back to austenite. Reversion was so rapid in all the studied steels that within 1 s most of the $\alpha'$-martensite disappeared (Fig. 6). The fast reversion suggests that it is of the shear type (Papers I and IV) [7,8]. Typical shear-reverted, highly dislocated austenite containing low-angle grain boundaries and having a lower image quality was visible with the aid of EBSD (Fig. 7). However, also fine, equiaxed austenite grains with random orientations were observed using EBSD (Fig. 7), suggesting that diffusion-aided nucleation of new grains and their growth had occurred. Therefore, it seems that both types of martensitic reversion tended to take place in annealing at 700 °C. Misra et al., [67] found that the presence of secondary precipitates did not influence the reversion mechanism in Cr-Ni-N steels. The same reversion mechanisms also occurred in the present Nb steels, as confirmed in Fig. 7. Nb alloying distinctly retarded reversion kinetics (Fig. 6). Sadeghpour et al. [96] also found a retarding effect of Ti alloying on reversion in 201L austenitic stainless steel and Baghbadorani et al. [12] found Nb-rich carbonitrides in 201 austenitic stainless steel. The slower reversion kinetics might be a result of fine precipitates whose size and density are suitable to obstruct the nucleation of new austenite grains in $\alpha'$-martensite, even though the driving force for the phase transformation is much higher than the pinning force created by the precipitates (Papers IV and V). However, all the $\alpha'$-martensite reverted back to austenite during heating at 200 °C/s up to 800 °C (Paper I).

Recrystallization of highly dislocated shear-reverted and retained austenite grains has been found to take place more slowly than reversion, i.e., at higher temperatures and over longer times, e.g., [9,74-76,97]. According to hardness measurements (Fig. 17), Nb alloying retarded the start and progress of recrystallization of RA, as annealing of 20, 100 and 200 s at 800 °C was required to recrystallize RA in the 0Nb, 0.11Nb and 0.45Nb steels, respectively (Paper IV). The retardation in the Nb steels can result from Nb atoms in the solid solution or Nb(C,N) precipitates, which are effective at pinning grain boundaries [98] and can even stop recrystallization in microalloyed carbon steels [99].

Recrystallization of RA grains tended to initiate both in deformation bands traversing large grains and on grain boundaries (Fig. 9), as also reported in the literature [74]. After reversion of martensitic areas, e.g., after annealing at 700 °C.
for 100 s, grain size was 300–400 nm (Fig. 8), but during longer annealing or annealing at higher temperature, where RA recrystallizes, ultrafine grains tended to grow. As a consequence of these two processes having different kinetics, grain size distribution became non-uniform in annealing at 800 °C for 1000 s (Fig. 10). Annealing at 900 °C resulted in quite uniform grain size distribution with a grain size of 1.4–1.9 μm (Fig. 11a–c), even though grain size was not as fine as when formed at a lower temperature. Anyhow, annealing for reversion and recrystallization of RA is an effective way to refine grain size, as uniform grain size decreased in the 0Nb steel from 18 to 1.9 μm as a result of the treatment.

Grain growth occurred during prolonged annealing at 900 °C or higher, as shown in Figs. 11d–f and 12, and Paper V. Nb alloying seems to be an effective means to obstruct grain coarsening, as 0.11 wt.% Nb was enough to retard grain growth at 1000 °C, and 0.28 wt.% at 1100 °C (Fig. 12). After 1000 s of annealing at 1100 °C, the grain size of the 0Nb steel was 59 μm but only 10 μm in the 0.28Nb steel. Therefore, a significantly finer grain size is achievable by alloying with Nb in the instance of annealing at high temperature for such a long time.

The lowest activation energy for grain growth in the studied steels was calculated for the 0Nb steel, 363 kJ/mol. The activation energy increased with Nb alloying up to 458 kJ/mol. This is what we would expect, as precipitates create a pinning stress on the grain boundaries, hindering their motion and thereby increasing the activation energy for grain growth (Paper V) [77,100,101]. Activation energy values ranging from 280 to 420 kJ/mol are reported in the literature for 321 and 347 austenitic stainless steels containing TiC and NbC carbides, respectively [80,81].

Grain size is controlled by competition between driving ($F_d$) and pinning ($F_p$) forces. By comparing the results predicted by FBM for $F_p$ and Zener’s equation for $F_d$, $F_p$ was higher until Nb alloying was at least 0.11 wt.%, suggesting grain growth in the 0Nb and 0.05Nb steels at 1100 °C (Fig. 14). For the 0.28Nb and 0.45Nb steels, $F_p$ was higher than $F_d$ and particles retarded grain coarsening. The $F_d$ of the 0.11Nb steel was slightly higher than the $F_p$ and some grain coarsening occurred at 1100 °C, as also observed in Fig. 12. Therefore, 0.28 wt.% Nb seems to be appropriate for reaching the maximum efficiency of alloying. Similarly, Sawada et al. [16] found that addition of 0.1 wt.% Nb is sufficient to retard grain coarsening at 900 °C in 301L austenitic stainless steel.
4.4 Nucleation and growth of ε- and α’-martensite during plastic deformation

Microstructure and austenite grain size affect the nucleation and growth of ε/α’-martensite during plastic deformation. It was noticed that the amount of α’-martensite formed in tensile straining was the lowest in the FG (4 μm) and MG-RA (1.5 μm) microstructures, Fig. 15. This diminishing trend is well reported in the literature, e.g., [102-108]. It has been argued that the stability is based on the energy associated with austenite to martensitic transformation [103,108]. Jin et al. [104] suggested that fine austenite grains have higher strength, which makes the shear transformation more difficult in them and therefore delays triggering of strain-induced martensitic transformation. The effective SFE also increases with decreasing grain size [105,106], which tends to increase the stability of the austenite phase.

In agreement with the present results, Maréchal [102] showed that at a given strain, the lowest amount of α’-martensite was formed in the instance of an austenite grain size of 0.9 μm in 301LN steel. With a larger or finer austenite grain size, the stability of austenite decreased, promoting martensite formation. In the tensile tests reported in Paper VI, during 20% straining only 4% α’-martensite was formed in the micron-scale MG-RA structure (Fig. 15), and in fact, even this α’-martensite was formed mainly in coarse RA grains (Fig. 16c). On the other hand, 12% α’-martensite was formed in the CG structure. However, in a microstructure comprising UFG-RA, the α’-martensite fractions were even higher than in the CG structure, so that 20% α’-martensite was formed in 20% straining. In the UFG-RA structure, RA grains were still heavily deformed with a high dislocation density, as evident from the high recorded hardness of 520 HV (Fig. 17), which promoted the transformation, and therefore α’-martensite was also formed in RA grains (Fig. 16). Also, in another study on 304L and 316L austenitic stainless steels, it has been proposed that the initial high dislocation density accelerates the formation of strain-induced martensite [57].

Somani et al. [9] also observed decreased stability of austenite in a refined grain structure in 301LN steel. This lower stability was observed and explained by Maréchal [102]. He showed that in grains smaller than 0.9 μm, martensite nucleates on grain boundaries and twins, while in coarser grains it nucleates at shear bands inside the grains. As a result of this change in the mechanism of martensite nucleation, it can become faster in CG structures as well as ultrafine structures.
It seems that in the UFG and MG structures, $\alpha'$-martensite nucleates straight from austenite without the intermediate step of ε-martensite formation, but in large RA grains and FG and CG structures the route can be either straight from austenite or sometimes via ε-martensite (Fig. 16a–c). As commonly reported in the literature, the amount of ε-martensite increases with strain up to a maximum, and then decreases with increasing plastic strain. For instance, Lee et al. [34] reported that the maximum amount of ε-martensite was obtained at 20% strain, after which the $\alpha'$-martensite started to form at the expense of ε-martensite in an Fe-18Cr-10Mn-N-C alloy.

For the FG, CG and RA structures, various nucleation sites of the $\alpha'$-martensite were seen, such as grain boundaries and slip or shear bands, intersection of deformation bands, including the bundles of stacking faults, dislocation pile-ups, deformation twins and plates of ε-martensite, some shown in Fig. 16, and also reported for Cr-Ni alloys [67,62,109].

The incidence of active deformation mechanisms, such as martensite formation, mechanical twinning and dislocation glide, are dependent on SFE. Curtze et al. [110] calculated the SFE of the 0Nb steel (204Cu) is 16.8 mJ/m². Saeed-Akbari et al. [111] estimated the decrease in effective SFE to be 4 mJ/m² for an increase in grain size from 5 to 20 μm. Therefore, in addition to $\alpha'$-martensite, both twinning and ε-martensite formation should be possible in the 0Nb steel. TEM examinations revealed twins and many extended dislocations close to or connected with grain boundaries in UFG and MG structures (Fig. 16d–f). Misra et al. [10] found that twinning facilitated nucleation of $\alpha'$-martensite in 301LN austenitic stainless steel in 100–500 nm grains by the emission of extended dislocations from grain boundaries.

4.5 Effect of microstructural evolution on mechanical properties

Grain refinement can be performed by cold rolling followed by subsequent reversion annealing. Obviously, the finest grain size is obtained by annealing a fully martensitic structure, e.g., [9-11,16,79,112-115], even though such a situation was not tested in this work. To keep this refined ultrafine grain size during practical industrial heat treatments, coarsening of the reverted grains must be prevented or at least retarded. As discussed above, this can be done by using nano-sized precipitates.

For the 0Nb steel, the highest yield strength of 1185 MPa and tensile strength of 1310 MPa with uniform elongation of 43% was achieved after annealing at
700 °C for 10 s (Fig. 19, Papers I, II and IV). The high yield strength is due to the complex microstructure consisting of unreverted tempered \( \alpha' \)-martensite, shear-reverted austenite with a high dislocation density and sub-boundaries, diffusion-reverted austenite with an ultrafine grain size (hardness of reverted grains 525 HV) and slightly recovered RA (hardness 520 HV), as discussed in Paper IV. However, to obtain better ductility, a longer annealing time is preferred.

For the 0Nb steel, after longer annealing at 700 °C, i.e., 100 s, \( \alpha' \)-martensite was reverted and the structure consisted of ultrafine new austenite grains with an average grain size (measured using LOM) of 0.5 \( \mu \)m and a hardness of 490 HV, and recovered, partially recrystallized RA grains with a hardness of 515 HV. Since the hardness of both constituents, UFG and RA, is almost the same, further straining produces \( \alpha' \)-martensite in both constituents. The stability of such a structure is low, as shown in Fig. 15, promoting \( \alpha' \)-martensite formation. Therefore, yield strength and tensile strengths are high, 900 and 1345 MPa, respectively, and uniform elongation is 38%.

For the 0Nb steel, features similar to those observed after annealing at 700 °C for 100 s were obtained after annealing at 800 °C for 10 s, except more recovery and recrystallization occurred in both reverted (440 HV) and RA (445 HV) grains. The grain size of the reverted grains increased from 0.5 to 1.5 \( \mu \)m (average grain size measured using LOM). The stability of such a structure is high due to the optimal grain size. As discussed above, with smaller or larger grain sizes the stability of the studied 0Nb steel decreased. Further straining promoted \( \alpha' \)-martensite formation mainly in RA (Fig. 15, Paper VI). Yield strength decreased to 540 MPa and tensile strength to 1065 MPa, but uniform elongation increased to 62%.

A uniform grain structure in the studied steels is achievable with 10 s of annealing at 900 °C. However, the grain size of reverted grains increases, although they are still micron-sized (Fig. 12). The stability of these fine grains (3 \( \mu \)m) is as high as in the above MG-RA structure (Fig. 15) and further straining promotes \( \alpha' \)-martensite formation in the largest grains. For the 0Nb steel, due to the presence of recrystallized grains, yield strength, tensile strength and uniform elongation are lower, i.e., 440 MPa, 1050 MPa, and 59% respectively, than in the non-uniform grain structure (540 MPa, 1065 MPa and 62%, respectively). Yield strength, tensile strength and uniform elongation are still higher than those of conventional annealed austenitic stainless steels, i.e., according to the Metals Handbook [116], typical values are 380 and 760 MPa, and 52% for 201, and 275 and 515 MPa, and 60% for 301.
According to the results, for the 0Nb steel the best combination of uniform elongation and yield strength is achieved with a composite structure (annealed at 800 °C for 10 s) consisting of fine grains and partially recovered RA, i.e., 62% and 540 MPa.

It seems that the highest austenite stability in the 0Nb steel is obtained with a grain size of 1.5–4 μm (measured using LOM). However, a structure with a uniform grain size of 1.5 μm (measured using LOM) was not achieved in the 0Nb steel due to the lack of a fully martensitic structure after cold rolling. However, by changing the alloy composition, a 100% martensitic structure is achievable, e.g., [9-11,79,112-115], but the highest austenite stability as a function of grain size may change.

In Fig. 20, data from the literature has been collected to compare the mechanical properties achieved in this study with some values reported for some Cr-Ni- and Cr-Mn-type austenitic stainless steels [4,9-11,79,113,114,117,118]. The strain rates vary between the steels, which obviously affects the results [62]. It is seen that Cr-Mn steels generally have a higher yield strength than Cr-Ni steels, but their ductility varies. The figure also shows that a wide range of mechanical properties is achievable via reversion treatment by controlling the heat treatment and thereby the microstructure. Nb alloying itself increases uniform elongation, but the main difference comes from variation of the microstructure and grain sizes, as discussed above. LOM images inserted in Fig. 20 display typical microstructures achieved via the reversion treatment of the studied steel with the corresponding mechanical properties.

Fig. 20 also shows data from the temper-rolled 0Nb steel [87,119]. It is seen that reversion is a more effective way to increase the combination of yield strength and uniform elongation than temper rolling.
The degree of grain size strengthening can be estimated from the Hall-Petch relationship between yield strength and grain size (Equation 5, Paper IV). Fig. 21 shows the experimental data and the fitted line for the 0Nb steel. The figure also shows the Hall-Petch plot of the yield strength of fine- and ultrafine-grained Cr-Ni and Cr-Mn austenitic stainless steels, the data were collected from the literature.

According to Fig. 21, the slope $k$ seems to be 256 MPa $\mu$m$^{-0.5}$ for the Cr-Ni steels [4,9,11,16,79,117]. This value is slightly higher than the 221 MPa $\mu$m$^{-0.5}$ obtained by Di Schino et al. [120] for 301LN, but much lower than the 495 MPa $\mu$m$^{-0.5}$ reported by Rajasekha et al. [4] for 304. However, based on this collected data, a distinctly higher slope of 367 MPa $\mu$m$^{-0.5}$ is obtained for the Cr-Mn type steels [97,112-115,118] than for the Cr-Ni steels. The $k$ of 377 MPa $\mu$m$^{-0.5}$ obtained
here for the 0Nb steel is in good agreement with this value. This analysis implies that a high Mn content increases grain size dependence. This is also supported by the fact that a high value of $k$, i.e., 350 MPa $\mu\text{m}^{-0.5}$, has been reported for 22% Mn TWIP steel [121]. Therefore, we can conclude that grain size strengthening is an important strengthening mechanism for austenitic stainless steels, even more so in the case of Cr-Mn steels than Cr-Ni steels.

It is seen that without RA, for the finest grain size of 1.4 $\mu$m (Table 4), the amount of grain size strengthening is 324 MPa, and for a grain size of 1.9 $\mu$m the value is 277 MPa. These high values emphasize the great importance of grain size refinement by reversion treatment in enhancing yield strength. As seen in Table 4, after annealing at 900 °C for 10 s, the experimentally measured yield strengths of 564 and 575 MPa for the Nb-alloyed 0.11Nb and 0.45Nb steels were 120–130 MPa higher than that of the 0Nb steel due to the contribution of precipitates.

**Fig. 21. Comparison of Hall-Petch analyses of the 0Nb steel, austenitic Cr-Ni [4,9-11,16,79,117] and Cr-Mn [97,112-115,118] stainless steels reported in the literature. [Paper IV, published by permission of Elsevier Ltd.]**

### 4.6 Recommendations for further research

In the present study, the relationship between annealing temperature and time in microstructure and mechanical properties were studied in 15Cr-9Mn-1Ni-2Cu austenitic stainless steels, some alloyed with Nb, in order to achieve better combinations of strength and elongation. However, the current study leaves room for further investigations as follows:

The reverted and partly recrystallized structure obtained here after annealing at 700 °C seems to provide an excellent strength-ductility balance. However, to limit the work involved, only a few experiments were carried out here. Therefore,
a more systematic study creating various microstructures consisting of tempered α’-martensite, reverted ultrafine austenite and recovered and partly recrystallized RA by annealing at a temperature of around 700–750 °C for various durations, and the dependence of strength-ductility combination on the fraction and condition of each microstructural component, should be performed. This could be done using Nb-free and Nb-alloyed steels.

In Paper II, the anisotropy of mechanical properties after 5, 12, 20 or 60 % cold rolling of the Nb-free steel was studied and discussed, as also seen in Table 3. However, the data series did not contain any Nb-alloyed steels. It is assumed that the behaviour of Nb-alloyed steel is similar to that of the Nb-free steel, but to confirm this, cold rolling and tensile tests should be performed.

In Paper III, the transformation from α’-martensite to austenite and the reversion temperature of the Nb-free steel were studied and discussed, as also seen in Figs. 4 and 5. However, the data series did not contain any Nb-alloyed steels. It is assumed that the behaviour of Nb-alloyed steel is similar to that of the Nb-free steel, but to confirm this, dilatometric studies together with XRD analysis should be performed.

Paper VI discussed the influence of austenite grain size and microstructure on strain-induced martensite transformation for the 0Nb steel, as also seen in Figs. 14 and 15. To thoroughly understand the differences in the kinetics of ε- and α’-martensite transformation between the 0Nb and Nb-alloyed steels, i.e., the nucleation sites of both types of martensite and their growth phenomena, interrupted tensile tests together with microstructural analysis, including XRD, EBSD and TEM work, are required. The results would also bring out new knowledge concerning the different behaviour of the steels during strain hardening and the effect of Nb alloying.

The corrosion properties of the “200-series” steels limit their applications. It is possible that sensitization due to precipitation tends to impair the intergranular corrosion resistance of ultrafine-grained steels. This was not tested in this study. Therefore, it would be necessary to perform corrosion tests for reversion-treated steels with a complex microstructure.

In Paper V the retardation of grain growth using Nb alloying was studied. In order to be able to use these steels in production, optimization of the process parameter window size of the studied steels using sensitivity analysis could be useful.
5 Summary and conclusions

The behaviour of metastable low-Ni high-Mn austenitic stainless steel 15Cr-9Mn-1Ni-2Cu, with and without Nb, was investigated in reversion annealing to determine the effect of the thermal history on the microstructure, grain size and mechanical properties. The aim of this study was to understand the relationship between the annealing cycle, the resultant microstructure and mechanical properties in order to achieve enhanced combinations of strength and ductility. The rate and mechanism of strain-induced martensite formation in different microstructures with different grain sizes under plastic straining were also studied. Reversion annealing after cold rolling was conducted on a Gleeble thermomechanical simulator and the microstructures were analysed using magnetic measurements, XRD, LOM, SEM-EBSD and TEM. Mechanical properties were tested using microhardness measurements and tensile tests. The main results and conclusions can be summarized as follows:

- In temper rolling, directional anisotropy in yield strength is formed in the Nb-free steel already at 5% thickness reduction. Strength is greater in the transverse direction than in the longitudinal direction. It was suggested that this is due to the dislocation structure, i.e., numerous stacking faults and activity in two slip systems. In reversion treatment, the anisotropy disappeared as the grain structure became fully softened. Anisotropy was also much reduced in a structure consisting of reverted grains and recovered RA without any α’-martensite.

- Upon fast heating, about 12% athermal martensite forms in cold-rolled steel at a temperature of around 550–700 °C and some isothermal martensite appears during holding. The dislocation density of α’-martensite decreases significantly due to tempering before reversion in a temperature range of 600–800 °C.

- Reversion from α’-martensite to austenite occurs rapidly at 700 °C in all the studied steels, even though Nb alloying retards the reversion. Features of both reversion types are present; large austenite grains with low EBSD image quality and low-angle grain boundaries of the shear type, and fine equiaxed grains of the diffusion type.

- Recrystallization of shear-reverted areas and retained austenite occurs at a higher temperature or during longer annealing than is the case for reversion.
At 800 °C the annealed microstructure becomes non-uniform due to the reversion forming ultrafine grains and recrystallization leading to coarser grains. Nb alloying retards the recrystallization kinetics of cold-rolled retained austenite.

A uniform austenite grain size of 2 μm was obtained on annealing at 900 °C for 10 s, being slightly finer in the Nb-alloyed steels than in the Nb-free one.

0.11 wt.% Nb alloying is sufficient to retard grain coarsening at least up to 1000 s at 1000 °C, but annealing at a higher temperature of 1100 °C requires 0.28 wt.%. This grain growth behaviour can be explained by the driving force predicted by Zener’s model and the pinning force predicted by the flexible boundary model.

A structure consisting of reverted grains and partially recrystallized austenite possesses significantly enhanced strength with high uniform elongation. Nb alloying further increases yield strength without reducing uniform elongation.

The transformation of strain-induced martensite in tensile straining depends on the original grain size. The stability of austenite is maximal in the instance of a fine grain size of about 1–4 μm, and stability decreases with an increase or decrease in grain size.

The nucleation sites of α'-martensite vary with grain size. In ultrafine grains, it nucleates on grain boundaries and mechanical twins. In coarser grains, α'-martensite nucleates straight from austenite or via ε-martensite at grain boundaries, shear bands and their intersections. In retained austenite, some deformation remains from cold rolling, so that further straining promotes martensite formation.
6 Novel features

To the best knowledge of the author, the following findings are original to this work:

- New $\alpha'$-martensite was formed in austenitic stainless steel upon fast, continuous heating before reversion.
- Both types of reversion mechanisms, shear and diffusion, occurred simultaneously during annealing at 700 and 800 °C. Nb alloying did not change the reversion mechanism, but retarded its rate.
- At 800 °C, the annealed microstructure became non-uniform due to the reversion forming ultrafine grains and recrystallization forming coarser grains, the effect being more pronounced without Nb alloying.
- The concentration of Nb required to prevent grain growth up to temperatures as high as 1100 °C was established as 0.28 wt.%. This was also confirmed using models to predict the driving and pinning forces for grain growth.
- $\alpha'$-martensite transformation in tensile tests depends in a complex way on grain size, but is also affected by cold-deformed, retained austenite grains. The increase in martensite volume fraction with increasing strain is greatest in a microstructure consisting of both ultrafine and retained austenite grains, being even faster in coarse-grained steel.
List of references


Original publications


Reprinted with permission from Yonsei University, Seoul, Korea (I), AIM Editorial Office (II), Trans Tech Publications Inc. (III), Elsevier Ltd. (IV), The Iron and Steel Institute of Japan (V) and Elsevier Ltd. (VI).

Original publications are not included in the electronic version of the dissertation.

553. Nelo, Mikko (2015) Inks based on inorganic nanomaterials for printed electronics applications


558. Aula, Matti (2016) Optical emission from electric arc furnaces

559. Ferdinand, Nuwan Suresh (2016) Low complexity lattice codes for communication networks

560. Xue, Qiang (2016) Analysis of near-optimal relaying schemes for wireless tandem and multicast relay networks


563. Huusko, Jarkko (2016) Communication performance prediction and link adaptation based on a statistical radio channel model

564. Nguyen, Vu Thuy Dan (2016) Transmission strategies for full-duplex multiuser MIMO communications systems

565. Keränen, Pekka (2016) High precision time-to-digital converters for applications requiring a wide measurement range

566. Koivuranta, Elisa (2016) Optical monitoring of flocs and filaments in the activated sludge process

567. Lohvikoski, Päivi (2016) Information processing in global virtual NPD projects

568. Kauppila, Osmo (2016) Integrated quality evaluation in higher education

Book orders:
Granum: Virtual book store
http://granum.uta.fi/granum/
Anna Kisko

MICROSTRUCTURE AND PROPERTIES OF REVERSION TREATED LOW-Ni HIGH-Mn AUSTENITIC STAINLESS STEELS